



Electrochemistry of Direct Carbon Fuel Cell Based on Metal Hydroxide Electrolyte

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General Feature of DCFC



- Electrochemical oxidation of Carbon is slow
 - High temperature operation needed
- Two approaches to accelerate the reaction:
 1. Solid Oxide Fuel Cell approach @ $\sim 1000\text{ }^{\circ}\text{C}$
 - *Modest results*
 2. Molten Electrolyte approach @ $< 800\text{ }^{\circ}\text{C}$
 - *Very Promising results*

DCFC with Molten Electrolytes



Hydroxide Electrolyte

- 1896 - by W. Jacques (the first DCFC tests)

Carbonate Electrolyte

- 1975 – by Weaver et al. @ SRI
- Late 1990's:
 - Hemmes et al. @ Delft University of Technology
 - Cooper et al. @ LLNL

Hydroxide Electrolyte (US Patent No. 6,200,697)

- 1995 - by SARA Inc.

Why Hydroxide Electrolyte?



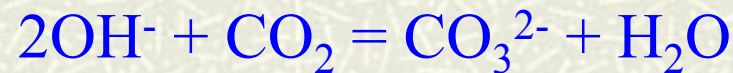
Advantages of Hydroxide electrolyte:

- **Higher electrical (ionic) conductivity.**
 - @ 450°C ~1.5X than in carbonates @ 650°C.
- **Higher electrochemical activity of carbon**
 - *i.e.* higher anodic currents and lower overpotentials
- **Lower operation temperatures**
- **Use of less expensive materials for cell fabrication**
 - Less expensive low carbon steels vs. expensive Inconel^R, Hastelloy^R and others
- **Higher efficiency of carbon oxidation**
 - At lower temperature dominant product is $\text{CO}_2 \Rightarrow 4e^-$ per C atom
 - vs. $\text{CO} \Rightarrow 2e^-$ at higher temperatures

Limitation of Hydroxide Electrolyte



- # Hydroxides were rejected in the past because they may absorb CO_2



- # Consequently losing the above advantages

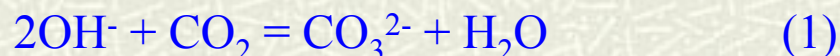
Q: Is there a means to overcome this problem?

A: Yes

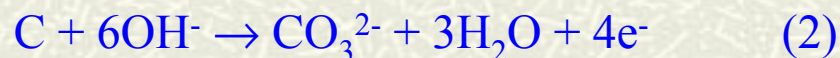
Hydroxide to Carbonate Conversion



Chemical formation of carbonate



Electrochemical formation of carbonate



Conversion may be prevented or reduced (**Patent Pending**)

- ✓ **if $c(\text{H}_2\text{O})$ is high** *i.e.* in acidic (hydrated) melt
 $\Rightarrow c(\text{O}^{2-}) = \text{low} \quad \Rightarrow c(\text{CO}_3^{2-}) = \text{low}$ - shown @ SARA
- ✓ In the presence of **oxides** (e.g. Mg, Sb, Si, ...) - to be shown
 - o MgO has already been proven by W. Jacques
- ✓ In the presence of **oxyanions** (pyrophosphate and persulfate)
- to be shown

High Water Concentration



Advantages of high water concentration in molten hydroxide

- Helps carbonate hydrolysis (reduces carbonate formation)
- Significantly increases ionic conductivity of the melt
- Significantly decreases corrosion of Ni, Fe and Cr (due to very low concentration of superoxide and peroxide ions)
- High $c(\text{H}_2\text{O})$ is easy to maintain by using humid air or (O_2)

SARA's Primary Objectives

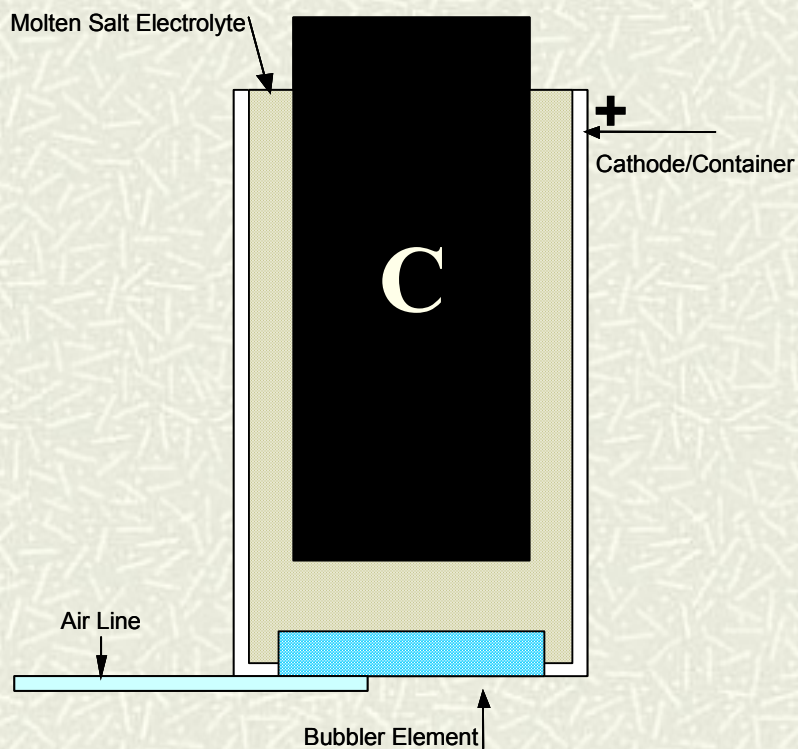


- # Simple cell design (non traditional fuel cell design)
 - Cylindrical geometry
 - Non-porous air cathode
- # Use of inexpensive materials
 - *e.g.* Fe₂Ti - Iron alloy with Titanium
 - Corrosion stable and catalytically active for O₂ reduction
 - Can be used for both cell container and air cathode **(Patent Pending)**
- # Performance acceptable for scale-up

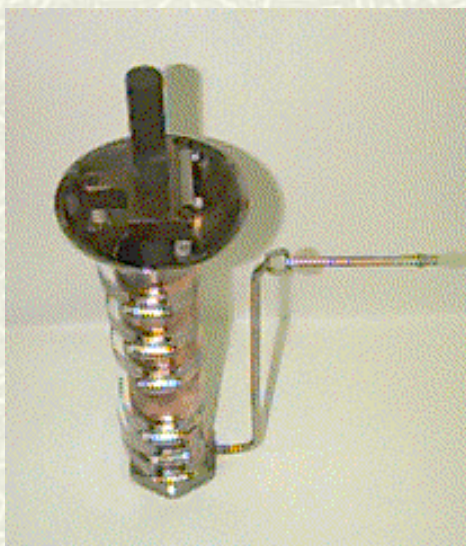
DCFC Design



**Design different than
traditional Fuel Cell**



Completed Cells



MARK II
26 cm² / 8 A

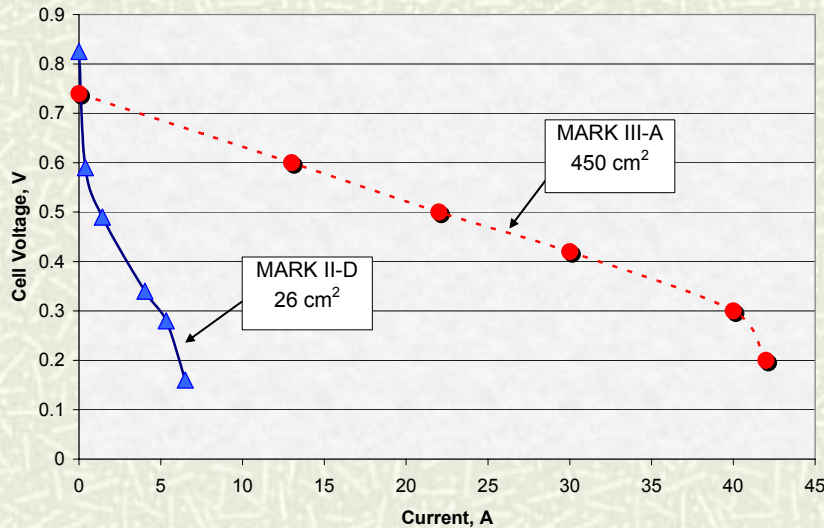


MARK III
450 cm² / 40 A

DCFC Test Results

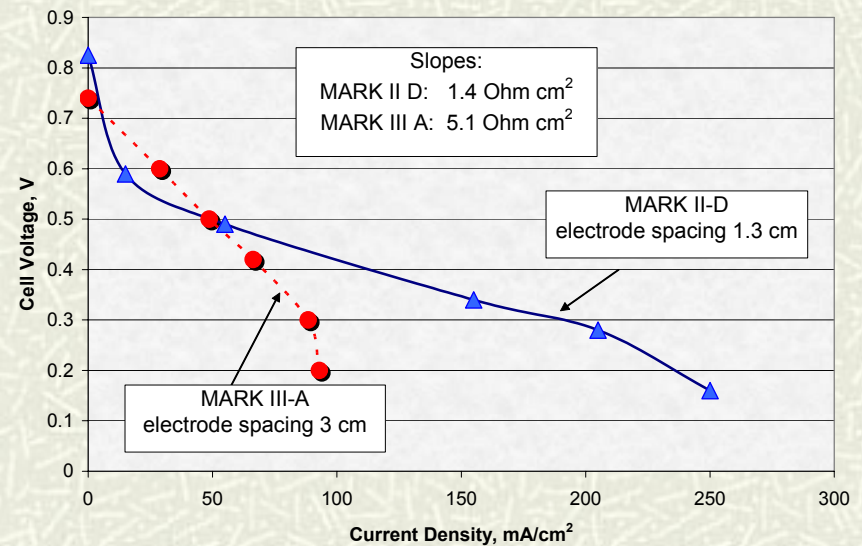


I-V curves for MARK II-D and MARK III-A DCFC



Bigger cell gives larger current

I-V curves for MARK II D and MARK III A DCFC



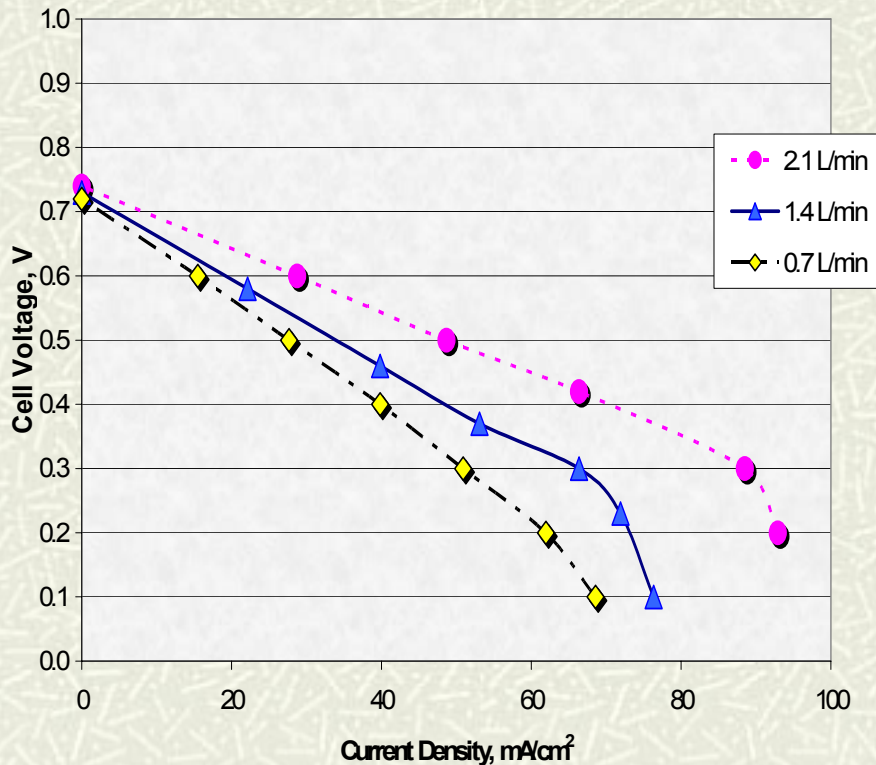
Smaller cell gives larger current density because of better design characteristics

DCFC Test Results (cont'd)



Cell Performance

I-V curves for MARK III-ADFC
at different air gas flow rates



Mixed Control

- Ohmic control
 - Large electrode spacing (3 cm)
- Mass transfer control
 - Limiting current due to O₂ reduction
- Low OCV (~0.75 V)
 - Anode collector design
- Use of Ti doped steel
 - eliminated need for lithiation of NiO cathode (**Patent Pending**)

DCFC Performance Improvements



Ohmic control

- Reduced electrode spacing
- Better current collector to anode contact

Mass transfer control

- Cathode with larger surface area
- Bubbling optimization (flow rate vs. bubble size)

Open Circuit Voltage

- Improved current collector-anode contact

Operation Voltage

- Use carbon anode instead of graphite (derived from coal)
- Graphite anode is the least active C-anode

Future Plan



In the next several months

➤ **Build new prototypes**

- MARK IV series with graphite anode and Fe₂Ti cathode

➤ **Carry out testing**

- **I-V curves for cell and electrodes**
- **Product gas analysis – efficiency & carbonization estimate**

Parameters:

- Temperature (300 °C – 700 °C)
- Dry and humid air and pure oxygen
- Gas bubbling rate
- Electrolyte composition
 - Single and mixed hydroxides Na, K, Li
 - Oxygen containing additives SiO₂, MgO, Sb₂O₃, Na₂S₂O₈, Na₄P₂O₇